Synthesis and Crystal Structure of 1,1′,2,2′-Bis(1,2,3-trithia-[3])ferrocenophane‡

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The first multiply chalcogen-bridged metallocene compound 1,1′,2,2′-bis(1,2,3-trithia-[3])ferrocenophane **1**, a species featuring two S_3 linkages around the metallocene nucleus, has been prepared by the lithiation of ferrocene 1,1′-dithiol, followed by treatment with elemental sulfur. The sulfur linkages lie in adjacent positions on the cyclopentadienyl rings and, in solution, the compound exists as a mixture of two diastereomers due to the orientation of the trisulfur bridges. Proton NMR spectra at ambient temperatures indicate the predominance of the chair–chair isomer **1a** (70%) over the less-favoured chair–boat species **1b** (30%). The structure of **1** has been determined by X-ray diffraction and the crystals are monoclinic, space group $P2_1/n$ with $a = 6.830(1)$, $b = 13.310(1)$, $c = 13.929(1)$ Å, $\beta = 99.70(1)°$ and $Z = 4$. Least-squares refinement give $R = 0.030$ for 1650 observed reflections whose intensities were measured on an area detector diffractometer with Mo-Kα radiation. The S–S bond lengths are 2.054(4), 2.065(4), 2.044(4) and 2.054(4) Å and the S(1)–S(2)–S(3) and S(4)–S(5)–S(6) bond angles are 105.1(2) and 103.5(2)° respectively. The S–C bond lengths are 1.752(6), 1.760(6), 1.752(6) and 1.755(6) Å with S–S–C bond angles of 102.3(2), 102.2(2), 102.4(3) and 101.8(2)°. The cyclopentadienyl rings are in an eclipsed conformation and are mutually parallel. The trisulfide linkages are in a chair–chair conformation with non-bonding separation of 3.25 and 3.23 Å for S(1) ··· S(3) and S(4) ··· S(6) respectively.

Much of the work in the area of formation of metallocenophanes has concentrated upon the use of methylene units as the bridging species. Most commonly, the bridging reaction has been an electrophilic acylation at the C_5H_5 ligand under acidic conditions. The bridges are normally trimethylene linkages though chains of two to ten organic bridging units have been prepared.[1–5] Known ferrocenophanes generally feature two or three methylene bridges around the same ferrocene unit although four, and perhaps, five bridges are thought to be possible.[6–11]

More recently, use of inorganic bridging units, such as main-group[12–16] and transition metals[17–21] and/or donor hetero-atoms *e.g.* chalcogens[22–27] and nitrogen-group elements,[28,29] has yielded much interest. [3]Ferro-, [3]rutheno- and [3]osmoceno-phanes containing trichalcogen bridges are known and several have been structurally characterised by X-ray diffraction.[25–27,30,31]

An overlap of both areas of research can now be demonstrated by reporting the synthesis and crystal structure of the first multiply chalcogen-bridged metallocenophane, namely 1,1′,2,2′-bis(1,2,3-trithia-[3]) ferrocenophane, a species involving two separate bridges of three sulfur atoms linking the two cyclopentadienyl rings.

The crystal structure of the compound is described and compared to analogous trimethylene- and trichalcogen-bridged species. Comment is also made as to the adjacent nature of the sulfur bridges in the compound and to the existence of two solution diastereomers as shown by ^1H NMR spectroscopy.

Results and Discussion

Synthesis.—Compound **1** was obtained in a 34% yield from the lithiation of ferrocene 1,1′-dithiol followed by addition of elemental sulfur and heating of the reaction mixture.

The orange–yellow crystals formed were air- and moisture-stable and withstood column chromatography on neutral grade II alumina. For characterisation, analytical, mass and NMR spectroscopy data were obtained in addition to an X-ray crystal determination (see later).

Attempts to form **1** *via* routes of (*a*) multiple lithiation of ferrocene using a large excess of butyllithium and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine or (*b*) using $[Fe(C_5H_4SLi)_2]\cdot 2thf$[32] (thf = tetrahydrofuran) as the starting material instead of ferrocene 1,1′-dithiol failed to give the desired product. Instead, the well known singly bridged species, 1,2,3-trithia-[3]ferrocenophane was the predominant product formed.

In the successful reaction, using ferrocene 1,1-dithiol and excess of butyllithium, it would be reasonable to expect to obtain mixtures of other bridged isomers resulting from di-, tri- and even penta-lithiated derivatives.[33] Traces of these presumed types of species were obtained but in insufficient amounts to warrant further study.

Substitution of the rings at the 1,1′ and 2,2′ positions caused these atoms to be the sites of the S_3 linkages between the rings. Initially, this was unexpected, since molecular models of the compound suggested that steric constraints would lead to 1,1′ and 3,3′ substitution. Therefore, there does seem to be some 'directive mechanism' driving the second substitution to the 2- or *ortho*-position on the rings. Evidence for such a mechanism can be found; in the metallation of alkyl-substituted ferrocenes, it has been shown that substitution in the 3 position is favoured over the 2 position by factors of 8 (for alkyl group, R = Me), 13 (R = Et), 32 (R = Pr^i) and 98 (R = Bu^t).[34,35] Obviously, this ratio increases significantly as the size of the alkyl group is increased, reflecting additional steric hindrance. The electronic

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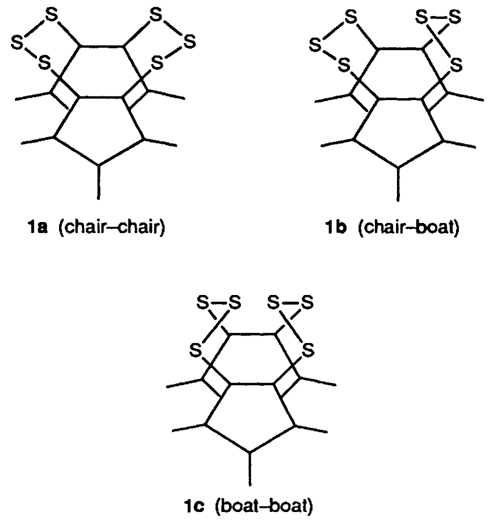
1a (chair–chair) **1b** (chair–boat)

1c (boat–boat)

Fig. 1 Diagram showing isomers **1a** (chair–chair), **1b** (chair–boat) and **1c** (boat–boat)

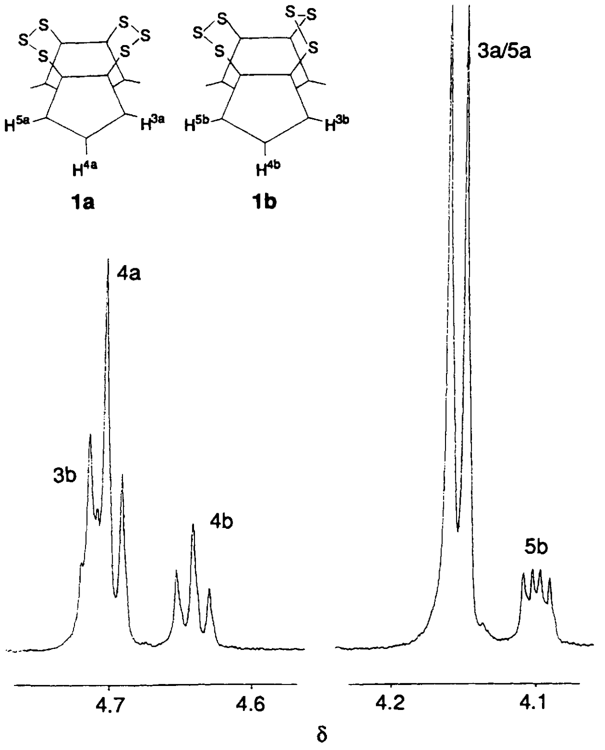

Fig. 2 Proton NMR spectrum of [Fe{[$(C_5H_3)S_3]_2$}] at 30 °C in $CDCl_2CDCl_2$

Table 1 Fractional atomic coordinates (× 10^4) for $C_{10}H_6FeS_6$ **1** *

Atom	*x*	*y*	*z*
Fe	1250.8(8)	2177.4(4)	2980.0(4)
S(1)	−1495(2)	3632(1)	4222(1)
S(2)	105(2)	4698(1)	3634(1)
S(3)	3028(2)	4323(1)	4101(1)
S(4)	4711(2)	2030(1)	5015(1)
S(5)	2991(2)	784(1)	5171(1)
S(6)	195(2)	1371(1)	5119(1)
C(1)	3318(6)	3263(3)	3384(3)
C(2)	2940(6)	3175(3)	2346(3)
C(3)	3389(6)	2180(4)	2102(3)
C(4)	4059(6)	1645(4)	2972(3)
C(5)	4019(6)	2299(3)	3770(3)
C(6)	−539(6)	1615(3)	3875(3)
C(7)	−540(6)	952(3)	3070(3)
C(8)	−1232(6)	1507(4)	2210(3)
C(9)	−1670(6)	2486(4)	2461(3)
C(10)	−1247(6)	2581(3)	3495(3)

* Estimated standard deviations (e.s.d.s) given in parentheses, are applicable to the least significant digits.

Table 2 Bond distances (Å) for $C_{10}H_6FeS_6$ **1** *

C(1)–Fe	2.032(6)	C(1)–S(3)	1.760(6)
C(2)–Fe	2.054(6)	C(5)–S(4)	1.755(6)
C(3)–Fe	2.056(6)	C(6)–S(6)	1.752(6)
C(4)–Fe	2.047(6)	C(10)–S(1)	1.752(6)
C(5)–Fe	2.028(6)	C(1)–C(2)	1.431(7)
C(6)–Fe	2.030(6)	C(2)–C(3)	1.414(7)
C(7)–Fe	2.056(6)	C(3)–C(4)	1.413(7)
C(8)–Fe	2.052(6)	C(4)–C(5)	1.416(7)
C(9)–Fe	2.045(6)	C(5)–C(1)	1.441(7)
C(10)–Fe	2.031(6)	C(6)–C(7)	1.427(7)
S(1)–S(2)	2.044(4)	C(7)–C(8)	1.419(7)
S(2)–S(3)	2.054(4)	C(8)–C(9)	1.394(8)
S(4)–S(5)	2.065(4)	C(9)–C(10)	1.425(7)
S(5)–S(6)	2.054(4)	C(10)–C(6)	1.442(7)

* E.s.d.s given in parentheses are applicable to the least significant digits.

or inductive influence of the various groups is also thought to have some effect.[36]

However, it was found that when the initial substituent was a $-PPh_2$ group, a lower than expected 3-position : 2-position ratio resulted, indicating that the substituent had some directing effect to the 2 position.[33]

Further evidence has been found from studies on the regioselective lithiation in π-arene systems. Apart from when steric hindrance is the overriding concern,[37] many nitrogen- and/or oxygen-containing substituents are lithiated in the 2- (or *ortho-*) position of the aromatic ring.[38–41] This has been attributed to an intramolecular co-ordination between the lithium atom and the lone pair of electrons in the substituent. Therefore, it seems that a similar type of interaction between lone pairs on the sulfur atom already on the ring and the incoming lithium is directing the metallation into the 2 position.

NMR Studies.—As **1** contains disubstituted cyclopentadienyl rings, with two trisulfide bridges, there is, in solution, the possibility of the existence of diastereomers as defined by the conformation of the S_3 linkages. This is illustrated in Fig. 1, where the isomers **1a** (featuring a chair–chair conformation) and **1b** (a chair–boat form) are shown (and additionally, **1c**, the undetected boat–boat form).

The presence of **1a** and **1b** in a ratio of approximately 70 : 30 is shown by examining the ^1H NMR spectrum of **1** taken at room temperature (Fig. 2). The signals 3a/5a (doublet) and 4a (triplet) relate to **1a**, whilst 5b (doublet of doublets), 4b (triplet) and 3b (doublet of doublets) arise from **1b**. Previous work[42–44] has shown the barrier to chair–chair interconversion or bridge reversal in singly chalcogen-bridged ferrocenophanes to be high, thereby permitting the observation of the diastereomers in solution at ambient temperature. A detailed discussion of the barriers to bridge reversal of this dibridged ferrocenophane is given elsewhere.[45]

X-Ray Structure.—Fractional atomic coordinates are given in Table 1 and a view of the molecule illustrating the numbering scheme is shown in Fig. 3. This displays the chair–chair conformation of the two trisulfide linkages (and is in accord with the NMR studies, where this conformer is the most populous species in solution).

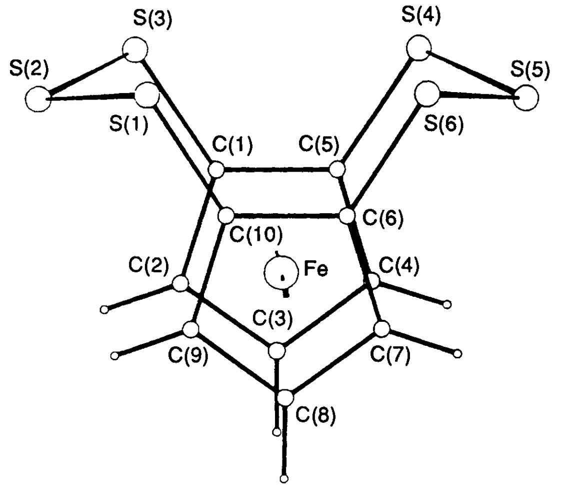

Fig. 3 A view of the X-ray crystal structure of $[Fe\{[(C_5H_3)S_3]_2\}]$ **1** showing the chair–chair configuration of the sulfur linkages

Table 3 Selected bond angles (°) for $C_{10}H_6FeS_6$ *

S(1)–S(2)–S(3)	105.1(2)	S(4)–S(5)–S(6)	103.5(2)
C(1)–S(3)–S(2)	102.2(2)	C(10)–S(1)–S(2)	102.3(2)
C(5)–S(4)–S(5)	101.8(2)	C(6)–S(6)–S(5)	102.4(3)
C(2)–C(1)–S(3)	128.4(4)	S(4)–C(5)–C(1)	124.5(4)
C(5)–C(1)–S(3)	124.4(4)	S(4)–C(5)–C(4)	127.8(4)
C(7)–C(6)–S(6)	128.6(4)	C(10)–C(6)–S(6)	123.4(4)
C(6)–C(10)–S(1)	123.9(4)	C(9)–C(10)–S(1)	129.2(4)
S(3)–C(1)–Fe	126.0(3)	S(6)–C(6)–Fe	125.1(3)
S(4)–C(5)–Fe	126.2(3)	S(1)–C(10)–Fe	125.7(3)
C(1)–C(2)–Fe	68.7(3)	C(4)–C(5)–Fe	70.4(3)
C(2)–C(3)–Fe	69.8(3)	C(5)–C(1)–Fe	69.0(3)
C(3)–C(4)–Fe	70.2(3)	C(4)–Fe–C(3)	40.3(2)
C(2)–Fe–C(1)	41.0(2)	C(5)–Fe–C(4)	40.7(2)
C(3)–Fe–C(2)	40.2(2)	C(4)–Fe–C(2)	68.1(3)
C(5)–Fe–C(3)	68.4(3)	C(3)–Fe–C(1)	68.5(3)
C(4)–Fe–C(1)	68.9(3)	C(5)–Fe–C(2)	69.0(3)
C(6)–Fe–C(1)	123.6(3)	C(10)–Fe–C(5)	123.3(3)
C(8)–Fe–C(2)	122.1(3)	C(6)–Fe–C(4)	122.5(3)
C(8)–Fe–C(4)	122.7(3)	C(10)–Fe–C(2)	123.1(3)
C(6)–Fe–C(3)	158.0(2)	C(8)–Fe–C(1)	158.2(2)
C(10)–Fe–C(3)	158.8(2)	C(8)–Fe–C(5)	158.7(2)
C(6)–Fe–C(2)	160.5(2)	C(10)–Fe–C(4)	159.6(2)
C(6)–Fe–C(5)	107.4(3)	C(8)–Fe–C(3)	107.3(3)
C(10)–Fe–C(1)	107.5(3)		

* E.s.d.s given in parentheses, are applicable to the least significant digits.

Bond distances and selected bond angles are listed in Tables 2 and 3 respectively. The carbon–carbon distances in the cyclopentadienyl rings vary from 1.394(8) to 1.442(7) Å whilst the C–C–C angles range between 106.8(5) and 109.3(5)°. Both parameters compare favourably with analogous ferrocenyl compounds,[20,25,30] as do the iron–carbon distances [2.028(6)–2.056(6) Å].

The S–S bond lengths show a slight asymmetry [2.044(4), 2.054(4), 2.054(4) and 2.065(4) Å] but are similar to those found in the singly trisulfur-bridged ferrocenophane[30] and osmocenophane.[27] The S–C bond lengths, ranging from 1.752(6) to 1.760(6) Å, are not unexpected whilst the virtually identical S–S–C angles [102.3(2), 102.2(2), 102.4(3) and 101.8(2)°] indicate an absence of bond angle strain within the molecule.[26] Differences in the ferrocenyl exocyclic C–C–S bond angles, C(6)–C(10)–S(1) and C(5)–C(1)–S(3) (mean 124.1°) and C(2)–C(1)–S(3) and C(7)–C(6)–S(6) (mean 128.5°), are observed and this asymmetry is a structural feature common to [3]metallocenophanes of this type.

The cyclopentadienyl rings adopt an eclipsed configuration and are virtually parallel. The two pairs of sulfur atoms are slightly displaced from the respective ring planes. The two S atoms, S(4) and S(6) are deviate more from the respective ring planes (0.014 and 0.022 Å) than S(1) and S(3) (0.005 and 0.003 Å), giving rise to a non-bonded separation of 3.234 Å for S(4) ⋯ S(6) shorter than 3.254 Å for the other pair S(1) ⋯ S(3), and consequently a more acute angle at S(4)–S(5)–S(6) [103.5(2)°] than at S(1)–S(2)–S(3) [105.1(2)°]. The non-bonding distances between the sulfide linkages are similar, being 3.386 Å for S(1) ⋯ S(6) and 3.430 Å for S(3) ⋯ S(4).

Further work is in progress on formation of similar mixed chalcogen-bridged metallocenophanes and investigating the co-ordinating properties of this potentially multidentate ligand system.

Experimental

General.—All preparations were carried out using standard Schlenk-tube techniques.[46] All solvents were freshly distilled, dried and degassed before use and all reactions were performed under purified nitrogen.

Proton NMR spectra were recorded on a Brüker AM250 FT spectrometer, operating at 250.13 MHz. The spectra were recorded as $CDCl_2CDCl_2$ solutions with the ^1H chemical shifts being quoted relative to $SiMe_4$ as internal standard. Mass spectra were recorded on a Kratos Profile spectrometer using the electron impact ionisation mode. Elemental analysis was performed by Butterworth Laboratories Ltd., Teddington, Middlesex.

Ferrocene 1,1′-dithiol was prepared by following a literature method.[22]

Preparation of Compound **1**.—Ferrocene 1,1′-dithiol (1.76 g, 7.0 mmol) was dissolved in diethyl ether (100 cm^3) and the stirred solution was treated with *N,N,N′,N′*-tetramethylethylenediamine (6.4 cm^3, 41.9 mmol), followed by butyllithium (26.2 cm^3, 1.6 mol dm^{-3}, 41.9 mmol) and the stirring was continued for 18 h. Sulfur flowers (2.15 g, 67.2 mmol) were added to the bright orange mixture and the suspension was refluxed for 6 h. Water (20 cm^3) was added to the cooled mixture which was then stirred for 30 min. The orange supernatant liquor was decanted and the solid residue extracted with hot hexane (3 × 30 cm^3) until the extracts were colourless. The combined liquor and extracts were dried over magnesium sulfate and filtered. Removal of solvent *in vacuo* gave a crude orange solid which was then subjected to dry column chromatography using neutral grade II alumina. Using hexane as eluent, an orange band was collected and shown to be 1,2,3-trithia-[3]ferrocenophane (0.39 g, 20%), m.p. 147–148 °C (lit.,[22] 149 °C). A second orange band was collected on elution with hexane–dichloromethane (1 : 1) and slow removal of solvent *in vacuo* gave orange microcrystals of $[Fe\{[C_5H_3(S_3)]_2\}]$ **1** (0.90 g, 34%), m.p. 220–225 °C (decomp.) (Found: C, 32.6; H, 1.8%; M^+ 374. $C_{10}H_6FeS_6$ requires C, 32.1; H, 1.6%; *M* 374); $\delta_H(CDCl_2CDCl_2)$ (chair–chair isomer, **1a**) 4.16 [2 H, d, $^3J(H^{3a,5a}H^{4a})$ 2.8, H^{3a}, H^{5a}] and 4.70 [1 H, t, $^3J(H^{4a}H^{3a,5a})$ 2.8 Hz, H^{4a}]; (chair–boat isomer, **1b**) 4.10 [1 H, dd, $^3J(H^{5b}H^{4b})$ 2.8, $^4J(H^{5b}H^{3b})$ 1.6, H^{5b}], 4.64 [1 H, t, $^3J(H^{4b}H^{5b,3b})$ 3.0, H^{4b}] and 4.71 [1 H, dd, $^3J(H^{3b}H^{4b})$ 3.0, $^4J(H^{3b}H^{5b})$ 1.6 Hz, H^{3b}]; *m/z* 374 (M^+, 100%), 310 (*M* − 2S, 35), 278 (*M* − 3S, 9), 246 (*M* − 4S, 21) and 182 (*M* − 6S, 18). [Crystals for X-ray diffraction were grown from slow evaporation of a solution of **1** in hexane–dichloromethane (1 : 1).] On further elution with hexane–dichloromethane (1 : 1) and then dichloromethane, other products were obtained but in insufficient amounts to be studied.

X-Ray Structure Determination.—*Crystal data.* $C_{10}H_6FeS_6$: *M* = 374.40, monoclinic, space group $P2_1/n$, a = 6.830(1), b = 13.310(1), c = 13.929(1) Å, α = 90, β = 99.70(1), γ =

90°, $U = 1248.14$ Å^3, $Z = 4$, $D_c = 1.992$ g cm^{-3}, $F(000) = 752$, $\lambda = 0.710\,69$, μ(Mo-Kα) = 21.425 cm^{-1}.

Data collection. Unit-cell parameters and intensity data were obtained by previously detailed procedures.[47] One hemisphere of data was collected with a detector swing angle of 17.95° and a crystal-to-detector distance of 40.45 mm. This corresponds to a full data set to a minimum θ_{max} value of 24°.

Solution and refinement of structure. The structure was solved by the application of routine heavy-atom methods (SHELX 84),[48] and refined by full-matrix least squares (SHELX 80).[49] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions in the final model. The F data were corrected for absorption using the DIFABS[50] procedure.

The final residuals R and R_G were 0.030 and 0.031 respectively for the 156 variables and 1650 reflections for which $F_o > 3\sigma(F_o)$. Atomic scattering factors and anomalous scattering parameters were taken from refs. 51 and 52 respectively. All computations were made on a T800 transputer hosted by an IBM compatible PC.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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